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(54) PROCESS AND APPARATUS FOR MANUFACTURING PREFORMED MOULDING MATERIALS

(71) We, CHEMISCHE WERKE ALBERT, a German Body Corporate of, Wiesbaden-Biebrich, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention relates to a process and apparatus for manufacturing preformed moulding materials. More particularly it povides a process and apparatus for the manufacture of dust-free sprayable, preformed moulding materials, which can be particularly easily and accurately metered, from hardenable synthetic resins, for example, phenol or melamine formaldehyde resins or unsaturated polyester resins, and conventional additives such as filler and/or reinforcing materials, lubricants or dyes. It makes possible the manufacture of moulding materials, which are particularly uniform as regards shape, size and physical and chemical properties.

According to a prior proposal the ingredients for moulding materials based on hardenable synthetic resins are initially treated in mixing and kneading apparatus and the resultant, generally hot, mixtures are then cooled and comminuted. The particle size is regulated e.g. by screening and classifying. As only a product in which the particle size is in a particular range can be used as a homogeneous end product, the relatively large amounts of oversize and/or undersize particles, e.g. between 30 and 5%, must be recycled to the comminution stage and/or the mixing stage. This enforced recycling of large quantities of material permits only an unsatisfactory utilisation of the capacity of the production equipment and thus increases the cost of the end product. Equally disadvantageous is the fact that the recycled product is subjected to further heat treatment in the mixing and kneading stage which must affect the condensation level of the resins, so that products are obtained which are heterogeneous as regards their flow and hardening characteristics. Close specifications as regards homogeneity and uniformity for all the characteristics important for the processing of the moulding materials to moulded articles can only be met to a limited extent with the known processes and only at considerable cost. In addition, a further tightening of these specifications can be expected as a result of the trend to automated and programmed processing.

It is an object of the invention to provide an improved process for manufacturing preformed moulding materials from hardenable synthetic resins and conventional additives.

According to the invention there is provided a process for the production of preformed moulding materials which comprises forming a mixture of hardenable synthetic resins and conventional additives, kneading the mixture in one or more stages until it has attained a sufficiently homogeneous and plastic state in which the components will not separate during subsequent treatment, forcing the mixture through a multi-orifice extrusion die by means of an axially movable feed screw or an equivalently acting means as herein defined, rotational movement of the feed screw being stopped or reduced while the mixture is being forced through the orifices of the extrusion die, and dividing the strands of material leaving the extrusion die into a substantially uniform granulate by chopper means.

By the expression "an equivalently acting means" we mean a feed screw which is not axially movable, in combination with a pressure chamber communicating with the housing of the feed screw at or adjacent the discharge end of said screw, the volume of said chamber being variable by means of a

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piston or similar device.

It is advantageous to cool the resulting granulate to enable it to be packed immediately. According to one embodiment of the invention, the mixture is kneaded and preferably cooled before being fed to the feed screw, such cooling being e.g. by contact or by evaporation of volatile components of the mixture. Such pre-kneading before feeding to the feed screw ensures better mixing of the components. Alternatively or in addition the kneaded mixture may be comminuteed before being fed to the feed screw. In the cooled mixture the condensation reaction is "frozen" and such mixture may be stored for long periods without deterioration.

According to another aspect of the present invention there is provided apparatus for performing the above process including a feed screw disposed in a housing and arranged to feed material to be preformed into a chamber having an outlet for said material wherein material fed by the rotation of the screw can be compacted, a multi-orifice extrusion die at or upstream of said outlet, chopper means downstream of said die, means for varying the speed of rotation of said feed screw, and means for varying the volume of said chamber so as to urge said material through said outlet, the said means for varying the speed of rotation and for varying said volume being adjustable independently of one another. Means for mixing and kneading as well as, if desired, a cooling and/or comminution means can be connected in series with the feed screw and the chopper means or crushing device for the granulate leaving the extrusion die and, if desired, a cooling and/or classifying means for the finished granulate can be connected at the outlet end of the feed screw.

In contrast to previously proposed processes for preparing granulates of thermosetting synthetic resins, the granulation is performed not by comminuting a solidified mixture but directly with a plastic mixture e.g. by passage through a perforated disc and then by dividing into substantially uniform pieces.

This process firstly offers the particular advantage that the proportion of particles of an incorrect size and fragments is extremely small. This proportion is generally below 1%, e.g. 0.1%. The production equipment can therefore work substantially without any burden of recycled material and without any loss of production. The small amounts of material to be recycled can be worked in without reducing the quality of the end product. Due to the small proportion of particles with an incorrect size classifying is generally not necessary.

A further advantage of the invention is the much simpler manufacturing process and the smaller size of the equipment involved. For the manufacturer of moulding materials a further significant advantage is that the time from which the mixture of the hardenable synthetic resins and the additives is subjected to heat until it becomes the preformed moulding material is at all times substantially constant, i.e. the so-called residence spread is particularly narrow. In other words the moulding materials produced according to the invention are particularly uniform as regards stucture and make-up and their reactivity because there are essentially no portions subjected to the action of heat for varying lengths of time which could result in differences in the condensation level and therefore in the flow and hardening characteristics, as has necessarily been the case when working according to the prior art due to the high proportions of material recycled.

The homogeneity of the hardenable moulding materials produced according to the invention is not only assured as regards their chemical composition, and therefore their processing characteristics, but also particularly as regards their external form, so that easy and reliable metering is possible. The granulate size can also be greatly influenced by the design of the extrusion die, e.g. as regards the orifice sizes and by the speed at which the chopper means operate, so that here again practically all requirements can be fulfilled.

A process of moulding, employing for example, a granulate from the plastic state, is no particular problem with thermoplastics such as polyethylene and polypropylene, because these thermoplastics remain plastic over a very wide temperature range, without undergoing any essential chemical changes. In addition, this process is reversible and can be repeated without difficulty.

On the other hand with hardenable moulding materials based on thermosetting synthetic resins the temperature range of plasticity is generally considerably narrower. On increasing the temperature as can also arise by mechanical processing, for example by kneading, the plastic state generally changes rapidly, frequently in an almost uncontrollable manner, into a chemically irreversible state characterised by incipient cross-linking which finally leads to irreversible three-dimensional cross-linking. For this reason many processes known for the processing of thermoplastics prove unsuccessful when used for preparing hardenable moulding materials, therefore much of the equipment used for preparing thermoplastics e.g. extruders cannot be used for forming hardenable moulding materials because the energy dissipated in the extruder by the screw and therefore the thermal energy

supplied to the material can scarcely be controlled and is mainly dependent on the resistance with which the orifice opposes the passage of material. In addition, heat regulation performed solely by conventional heating and cooling means functions much too slowly to be able to maintain sufficiently reliably the narrow temperature range of the plastic state in the case of hardenable moulding materials.

In the present invention, it is necessary to knead the mixture before granulation to ensure that the resin and additives do not separate (demix) when extrusion pressure is applied resulting in extrusion of the resin component alone while the solid additives remain upstream of the extrusion die. The kneading must be performed to ensure that the resin is deposited on the solid additives to form a homogeneous and plastic mixture from which the components will not separate during subsequent treatment.

The invention is illustrated diagrammatically in the accompanying drawings, which illustrate different variants of the preliminary treatment of the starting materials.

In the accompanying drawings:—

Figure I is a flow diagram of a process in which the preparation of the material fed to the feed screw is effected by mixing and/or preplasticising.

Figure II is a flow diagram of a process in which the aforementioned preparation is effected by mixing and repeated kneading controlled by intermediate cooling, the cooling taking place by evaporation; and

Figure III is a flow diagram of a process which is a variation of that shown in Fig. I.

In these three embodiments the material so prepared or pretreated is kneaded and preformed in a feed screw granulation apparatus, subsequently cooled and, if desired, classified; and

Figure IV is a partially cross-sectional view of a single-spindle, axially movable feed screw granulation apparatus according to the invention.

Figure V illustrates in plan and partial sectional view apparatus including the aforementioned "equivalently acting means" comprising a chamber 22 linked with the housing 12 of the feed screw 11. The volume of the chamber 22 is variable by means of the piston 23 which may be actuated e.g. by hydraulic or pneumatic cylinder 24. Referring now to figures I to III, the various blocks of the flow diagram represent:

1 and 2, mixing states e.g. cascade mixers, i.e. a parallel or series-connected group of mixers which, if desired, can also perform kneading, preplasticising and cooling functions;

3, a kneading stage, for example a mixing roller or a screw kneader;

4, a cooling stage, for example, a moving surface cooler belt or vibration cooler;

5, a comminution stage, for example crushers or mills;

6, a kneading and granulating stage according to the invention, e.g. a single-spindle feed screw as shown in Figure IV or a similar apparatus according to Figure II (or Figure V);

7, a cooling stage for the granulate, for example a moving surface cooler, spray cooler or fluidised bed cooler and

8, a classifying stage for separating particles of incorrect size, for example a screening machine.

The process shown in Figures I-III can be performed in various ways:

a) In mixing stages 1 and 2 (Figure III) the starting materials are thoroughly mixed with one another. The mixture is then supplied directly to the feed screw 6 (i.e. omitting stages 3, 4 and 5 of Figure I) and therein, i.e. in the kneading and granulating stage, is converted into the plastic state and in this state forced through the extrusion die and divided up into substantially uniform lengths by chopper means. The granulate is then cooled in stage 7. If desired, in stage 8, as already stated, the very small proportion of undersize and oversize particles is screened out and can without difficulty be recycled to the granulation state 6, following the dotted arrow. The dotted representation of stage 8 signifies that the screening and recycling do not represent a necessary but only an optional measure.

b) In the same apparatus shown in Fig. I the mixture of starting materials can, however, be partially plasticised by kneading in stage 3 and cooled, for example, by contact and/or air cooling in stage 4 before it is supplied directly to the kneading and granulation stage 6, i.e. the feed screw and there processed further.

c) In the same apparatus shown in Fig. I, the starting materials are mixed in stages 1 and 2, kneaded in stage 3, cooled until the material solidifies in stage 4 and in stage 5 comminuteed to a granular state suitable for the subsequent treatment. Working stage 6 again employs a single-spindle axially movable feed screw as the kneading and granulating stage. The granulate obtained is cooled in stage 7, and in stage 8, if desired, incorrectly sized particles are classified and subsequently recycled to stage 6. This split working process makes possible the arrangement of a "material buffer", i.e. a certain reserve of material which has passed through the comminution stage 5 and can be gradually fed to the granulation stage 6.

In the process according to Fig. II the starting materials are initially mixed with one another in mixing stages 1 and 2. The mixture then passes into kneading stage 3

which in the present case is in the form of a twin screw and may also be provided with vapour removal means if cooling is to be performed by vapourising volatile starting materials. This cooling can, however, also take place between the kneading stage 3 and the kneading and granulation stage 6. As shown, the stage 6 can also comprise a plurality of parallel-connected, single spindle feed screws to ensure a continuous transfer of the prekneaded material from stage 3 to stage 6 to provide increased throughput.

Figure IV illustrates an embodiment of a single-spindle feed screw (stage 6). The screw 11 of this apparatus is mounted so as to be rotatable and axially movable as shown by the arrows in housing 12 communicating with chamber 21 at its outlet end. At the outlet from chamber 21 is arranged a multi-orifice extrusion die 13 with a chopper blade 14. The housing 12 has a heating and/or cooling jacket 15 with a number of temperature zones. The screw 11 has a central duct 16 for the passage of the heating or cooling agent. These devices serve to compensate heat losses but can also be used to match the frictional conditions on the housing wall to those on the screw surface. The screw shaft is driven continuously via a gear which may be infinitely variable as desired.

The screw length is usually between 5 and 25 times the screw diameter. The peripheral speed of the screw can, for example, vary in the range 0.1 to 40m/min corresponding e.g. with a screw diameter of 120 mm to a speed range of 0.25 to 105 r.p.m.

The axial movement (thrust stroke) is adjustable independently of the speed of rotation, e.g. over the range 0.1 to 3, say. 0.25 to 3 times the screw diameter. The dynamic pressure can be adjusted as desired between 1 and 100 kp/cm².

By means of the heating and cooling control unit (18) the temperature of the housing can be regulated in zones and the temperature of the screw regulated independently thereof. The control means may control independently the temperature of said feed screw and of a plurality of zones of the housing of said feed screw and said chamber. The temperature and/or pressure sensors (19) are used to check and control the characteristic variable state of the material. Conventional mechanical, electrical and hydraulic means control the dynamic pressure indicated at 17, the screw speed indicated at 20 and the speed of axial movement.

When operating the feed screw a growing "cushion" of material builds up in chamber 21 between the end of the screw and the granulating head. When this cushion attains a length determinable by a limit switch, it is forced through the granulating head. At the thrust necessary for this purpose, the screw acts as a piston with the rotational movement stopped or reduced. The speed of the thrust is controllable independently of the extrusion pressure. The kneading process and therefore the heat supply to the moulding compound is interrupted on discharge or at least considerably reduced.

The most important components of the granulating means 13 are a multi-orifice extrusion die and a cutting or chopping means. The synchronisation of e.g. the blade speed and the thrust speed makes possible the production of a granulate of uniform length. The cross-sectional shape of the granulate is determined by the shape of the orifices in the perforated plate. The cooling means which in certain circumstances is arranged downstream of the granulating means cools the granulate material to such an extent that it can be packed.

A classifying apparatus can be used for separating the small amounts of broken granulate.

In order that the invention may be better understood the following examples are given by way of illustration only:—

Example 1

With reference to Figure I, 380kg of a resin with a melting point of 60°C, prepared from phenol and formaldehyde in a molar ratio 1:0.9 are homogeneously mixed in a pulverulent condition in a cascade mixer (1,2) with 40kg of hexamethylene tetramine, 40 kg of ground kaolin, 10kg of zinc stearate, 5kg of ester wax with a drop-forming temperature of 90 to 100°C, 2.5kg of a nigrosin base dissolved in methanol and 522.5 kg of predried sawdust. This mixture is then plasticised, homogenised and compressed in a screw kneader (3). The mass thus obtained is then cooled in a vibration cooler (4) and comminuted in a cross-beater mill (5) to a granular condition suitable for the subsequent treatment. In the thrust screw granulating machine (6) the compressed mass is plasticised by kneading under controlled dynamic pressure and, with a stationary or reduced rotational movement of the screw is forced by axial movement of the screw through the granulating head and the chopping means and thus formed into a cylindrical granulate with a diameter of 3mm and a length of 3mm. The granulate is cooled in a vibration cooler (7) to permit its immediate packing.

The granulated material is in an essentially dust-free form, has excellent friability characteristics and due to its homgeneous geometrical structure can be satisfactorily metered. The material produced according to the invention can be processed to moulded articles of satisfactory quality by the con-

ventional moulding and transfer moulding methods but with particular advantage on automatically functioning injection moulding machines.

Testing of the material according to DIN 7708, sheet 2 provides the following values:—

Bending strength (kp/cm^2)	840
Impact resistance (kpcm/cm^2)	7.0
Notch impact resistance (kpcm/cm^2)	1.8
Resistance to deformation by heat according to Martens (°C)	131
Glow resistance (quality degree)	3
Water absorption (mg)	62
Surface resistance (treated) (comparative figure)	10
Actual density (g/cm^3)	1.4
Bulk density (g/cm^3)	0.74
Moisture content (%)	2.0

Example 2

510 kg of a melamine resin based on melamine and formaldehyde in the molar ratio 1:2.2 which has been condensed and subsequently spray-dried, having a melting range of 70-80°C, are thoroughly mixed in a cascade mixer (1,2) with 8 kg of calcium stearate, 6.5 kg of ester wax with a drop-forming temperature of 90-100°C, 20.5 kg of titanium dioxide and 455 kg of sawdust and, according to the flow diagram shown in Fig. I are hot-mixed, pre-plasticised, cooled, comminuted and formed according to the invention into a cylindrical granulate with a diameter of 2.5 mm and a length of 2mm. The granulate is homogeneous and is cooled in a vibrationcooler.

The granulate is practically competlely dust-free, friable and can be satisfactorily metered.

The material so prepared according to the invention can be automatically processed to form moulded articles of satisfactory quality by both transfer moulding and injection moulding.

Testing according to DIN 7708, sheet 2 yields the following values:—

Bending strength (kp/cm^2)	815
Impact resistance (kpcm/cm^2)	6.0
Notch impact restistance (kpcm/cm^2)	1.9
Resistance to deformation by heat according to Martens (°C)	130
Glow resistance (quality degree)	3
Water absorption (mg)	132
Surface resistance (treated) (comparative figure)	11
Creep current resistance (stage)	KA 3c
Actual density (g/cm^3)	1.5
Bulk density (g/cm^3)	0.77
Moisture content (%)	2.3

250 kg of an unsaturated polyester based on 188.9 kg of fumaric acid, 15.5 kg of adipic acid and 107.6 kg of ethylene glycol, with a melting point of 90 to 95°C, are thoroughly mixed with 50 kg of diallyl phthalate, 10 kg of tert. butyl perbenzoate, 15 kg of zinc stearate, 10 kg of titanium dioxide, 10 kg of barium sulphate, 100 kg of cut 3mm glass fibres (surface-treated with silane to improve adhesion to the resin) and 565 kg of limestone in a cascade mixer (1,2) in Figure I. This mixture is then plasticised, homogenised and compressed on a set of mixing rollers (3). The material thus obtained is subsequently cooled on a belt cooler (4) and comminuted in a cutting mill (5) to a granular state suitable for subsequent treatment. In the axially movable feed screw granulating machine (6) the compact mass of material is plasticised by kneading and with rotational movement of the screw stopped is forced by axial movement of the screw through the granulating head and chopping means and formed into a cylindrical granulate with a diameter of 3mm and a length of 3mm. The granulate is homogeneous and is cooled in a vibration-cooler.

The granulate is completely dust-free, friable and can be satisfactorily metered.

Testing according to DIN 7708, sheet 2, yields the following values.

Bending strength (kp/cm^2)	875
Impact resistance (kpcm/cm^2)	6.8
Notch impact resistance (kpcm/cm^2)	3.1
Resistance to deformation by heat according to Martens (°C)	142
Glow resistance (quality degree)	3
Water absorption (mg)	27
Surface resistance (treated) (comparative figure)	13
Specific resistance (Ohm.cm)	1.4×10^{14}
Dielectric loss factor (tgδ)	0.010
Dielectric strength (kV/cm)	134
Creep current resistance (stage)	ka 3c
Actual density (g/cm^3)	2.0
Bulk density (g/cm^3)	0.88
Moisture content (%)	0.4

WHAT WE CLAIM IS:—

1. A process for the production of preformed moulding materials which comprises forming a mixture of hardenable synthetic resins and conventional additives, kneading the mixture in one or more stages until it has attained a sufficiently homogeneous and plastic state in which the components will not separate during subsequent treatment, forcing the mixture through a multi-orifice extrusion die by means of an axially movable feed screw or an equivalently acting means as herein defined, rotational movement of the feed screw being stopped or

reduced while the mixture is being forced through the orifices of the extrusion die, and dividing the strands of material leaving the extrusion die into a substantially uniform granulate by chopper means.

2. A process according to claim 1 in which the resulting granulate is cooled.

3. A process according to claims 1 or 2 in which the mixture is kneaded before being fed to the feed screw.

4. A process according to claim 3 in which said kneaded mixture is cooled before being fed to the feed screw.

5. A process according to claim 4 in which said cooling is effected by contact or evaporation of volatile components of the mixture.

6. A process according to any one of the claims 3-5 in which the kneaded mixture is comminuted before being fed to the feed screw.

7. A process according to any one of the preceding claims in which the granulate is classified and in which the oversized and undersized fractions are recycled.

8. A process according to any one of the preceding claims in which the peripheral speed of the feed screw is 0.1 to 40 m/min.

9. A process according to any one of the preceding claims in which the thrust stroke of the axially movable feed screw is adjustable in the range of 0.1 to 3 screw diameters.

10. A process according to claim 9 in which the thrust stroke of the axially movable feed screw is adjustable in the range of 0.25 to 3 screw diameters.

11. A process according to any one of the preceding claims in which the dynamic pressure during the plasticising step is in the range of 1 to 100 kp/cm^2.

12. A process for the production of preformed moulding materials, substantially as hereinbefore described with reference to any one of Figs. I-III of the accompanying drawings or to any one of the Examples.

13. Apparatus for carrying out the process claimed in claim 1 comprising a feed screw disposed in a housing and arranged to feed material to be preformed into a chamber having an outlet for said material wherein material fed by the rotation of the screw can be compacted, a multi-orifice extrusion die at or upstream of said outlet, chopper means downstream of said die, means for varying the speed of rotation of said feed screw and means for varying the volume of said chamber so as to urge said material through said outlet, the said means for varying the speed of rotation and for varying said volume being adjustable independently of one another.

14. Apparatus according to claim 13 in which said means for varying the volume of said chamhber are provided by means for axially moving said feed screw into said chamber.

15. Apparatus according to claim 14 in which the range of said axial movement is 0.1 to 3 times the diameter of the feed screw.

16. Apparatus according to claim 14 in which the range of said axial movement is 0.25 to 3 times the diameter of the feed screw.

17. Apparatus according to claim 13 in which said means for varying the volume of said chamber comprise a piston.

18. Apparatus according to any one of claims 13-17 including means for controlling independently the temperature of said feed screw and of a plurality of zones of the housing of said feed screw and said chamber.

19. Apparatus according to any one of claims 13-18 in which the rotational speed of the feed screw is adjustable within the range of 0.25 to 105 r.p.m.

20. Apparatus according to any one of claims 13 to 19 in association with mixing and kneading means arranged to feed material to said feed screw.

21. Apparatus according to claim 20 including cooling and/or comminution means arranged between said mixing and kneading means and said feed screw.

22. Apparatus according to any one of claims 13-21 in association with separating means, cooling means and/or classifying means for the granulated product.

23. Apparatus for the production of preformed molding material, substantially as hereinbefore described and as illustrated in Figs. IV or V of the accompanying drawings.

24. Preformed moulding materials whenever produced by a process as claimed in any one of claims 1-12 or by apparatus as claimed in any one of claims 13-23.

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Fig. I.

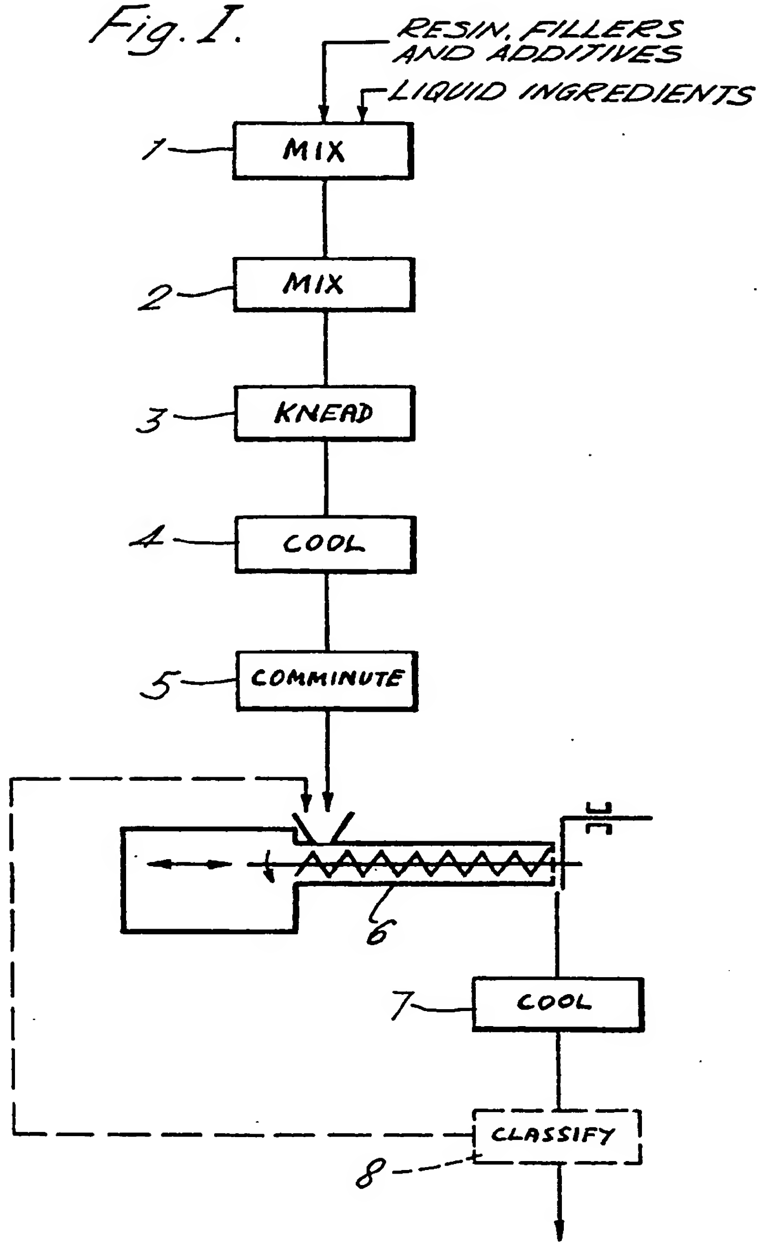
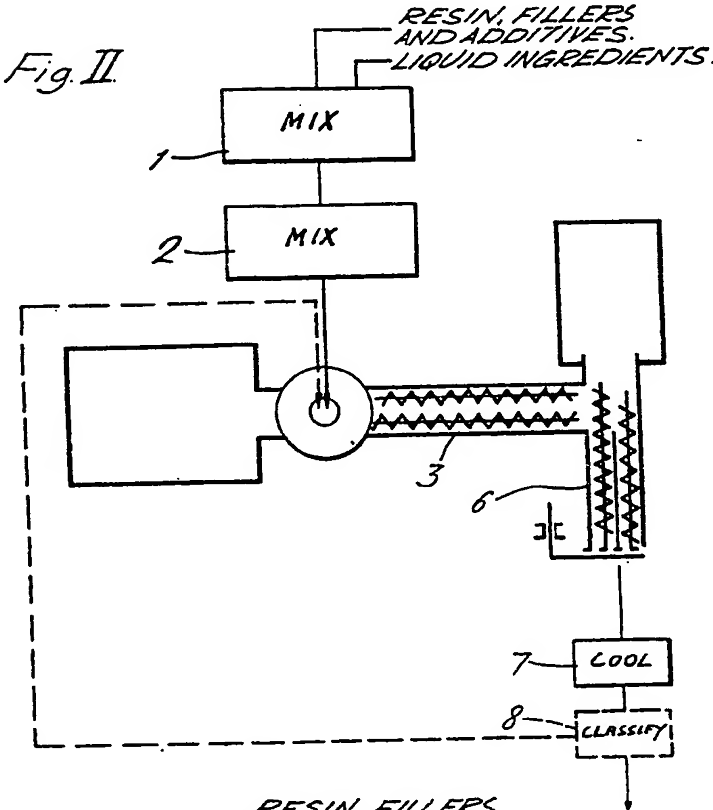

RESIN, FILLERS AND ADDITIVES
LIQUID INGREDIENTS
1
MIX
2
MIX
3
KNEAD
4
COOL
5
COMMINUTE
6
7
COOL
8
CLASSIFY

Fig. II



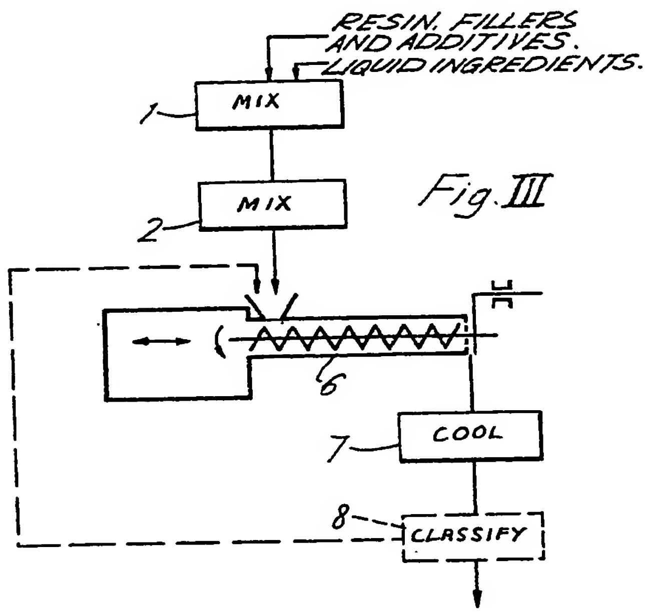


Fig. III

This drawing is a reproduction of the Original on a reduced scale.
SHEET 3

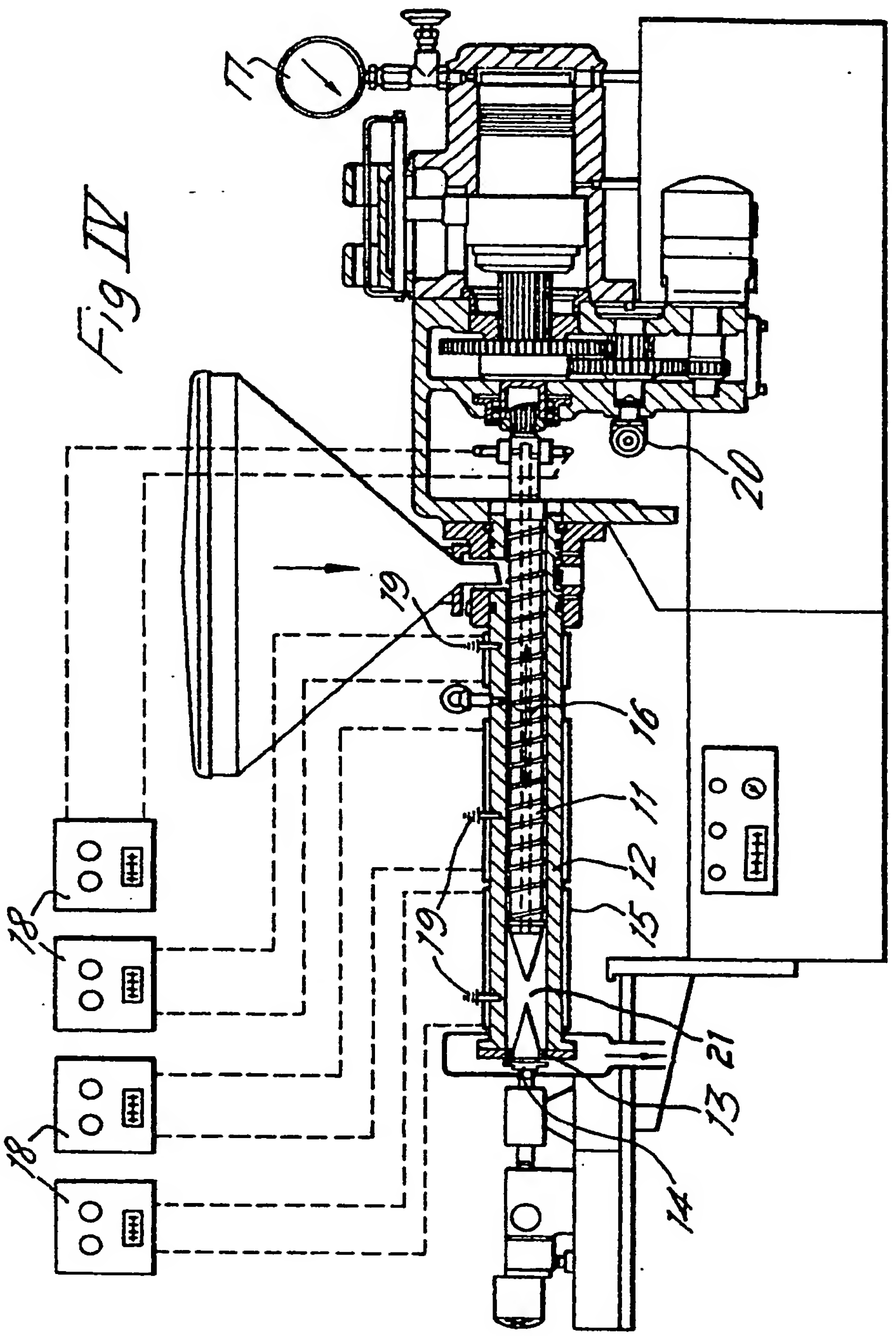


Fig IV

Fig. V